SCIENCE CHINA
Chemistry

•HIGHLIGHTS•

July 2025 Vol.68 No.7: 2782–2783
https://doi.org/10.1007/s11426-025-2635-2

Bilayer solid electrolyte interphase for stable lithium metal batteries

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Received March 6, 2025; accepted March 10, 2025; published online April 21, 2025

Citation: Zheng Z, Zhang Q. Bilayer solid electrolyte interphase for stable lithium metal batteries. *Sci China Chem*, 2025, 68: 2782–2783, https://doi.org/10.1007/s11426-025-2635-2

Lithium (Li) metal battery is regarded as a promising candidate in pursuit of high-energy-density secondary batteries [1]. However, Li metal batteries suffer from rapid capacity decay and anxious safety concerns, primarily due to non-uniform Li plating/stripping [2]. Derived from the spontaneous reduction decomposition of electrolytes, solid electrolyte interphase (SEI) acts as the passivation layer between electrolytes and Li metal anodes, of which the Li ions transport property and stability have a great impact on the uniformity of Li plating/stripping. Consequently, constructing a robust SEI is crucial to improve the stability of Li metal anodes and further achieve long-cycling Li metal batteries.

A robust SEI should possess high ionic conductivity and excellent electronic insulativity [3]. Moreover, electrochemistry stability, mechanical stability, and homogeneity, have been identified as being closely associated with the performance of Li metal batteries [4]. Tremendous efforts, mainly based on electrolyte design, have been dedicated to regulating SEI components and structure to construct a robust SEI [5–7]. Accordingly, the cycle life of Li metal batteries has been increased gradually. However, the cycle stability of Li metal anodes under high-rate charging and discharging conditions is still a challenging yet essential task.

In *Nature*, Yan, Li, Guo, Tao, and co-workers [8] reported *t*-Li_2ZrF_6 (trigonal)-rich bilayer SEI that markedly enhances Li ion transfer and suppresses the growth of Li dendrites, further boosting the cycle stability of Li metal batteries under high-rate charging/discharging process. For the construction of *t*-Li_2ZrF_6-rich SEI, a voltage-driven electrolyte additive, *m*-Li_2ZrF_6 (trigonal) particles, was developed. Under the drive of the electric field, *m*-Li_2ZrF_6 particles can release a large number of ZrF_6^{2-} ions into the electrolyte, contributing to the *in-situ* formation of an SEI enriched with *t*-Li_2ZrF_6 crystals on Li metal anodes. The electronic insulativity of *t*-Li_2ZrF_6 can block electron tunnelling, thereby suppressing continual electrolyte decomposition during cycles. Furthermore, the excellent Li^+ transport characteristics and abundant lithiophilic sites on the *t*-Li_2ZrF_6-rich SEI can enhance the Li^+ transport rate and promote uniform Li deposition. Moreover, benefiting from the characteristic of voltage-driven dissociation and release of ZrF_6^{2-} ions, the *m*-Li_2ZrF_6 additive can promptly repair the damaged SEI and retard the depletion during cycles, which is the common shortcoming of traditional additives, thereby enabling Li metal anodes stable over the long cycling. Therefore, the SEI enriched with *t*-Li_2ZrF_6 exhibits the three essential characteristics of an ideal SEI, including high ionic conductivity, excellent electronic insulativity, and great electrochemical stability. Owing to the excellent properties of *t*-Li_2ZrF_6-rich SEI, Li metal battery assembled with $LiFePO_4$ cathode (areal loading, 1.8/2.2 mAh cm^{-2}), three-dimensional Li-carbon anode

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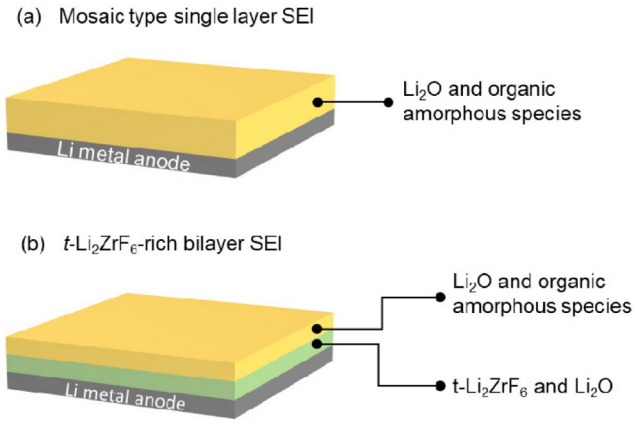

Figure 1 (Color online) Schematic diagram of (a) common single-layer SEI structure and (b) *t*-Li_2ZrF_6-rich bilayer SEI on Li metal anodes.

(50-μm-thick Li), and *m*-Li_2ZrF_6-based electrolyte displays greatly improved cycle stability with high capacity retention (>80.0%) after 3,000 cycles with 1 C/2 C charging/discharging rate.

In summary, a long cycle life under high rates has been achieved in Li metal coin cells with *t*-Li_2ZrF_6-rich SEI. Subsequently, the evaluation of the effectiveness of *t*-Li_2ZrF_6-rich SEI in high-energy-density (>400 Wh kg^{-1}) pouch cells is necessary, which is the key step for the practical applications of Li metal batteries. The present approach to SEI design is predominantly reliant upon the trial-and-error method of electrolyte design, a process that is both time-consuming and inefficient. The primary obstacle to achieving rational SEI design is the incomplete understanding of the SEI itself, primarily due to the ambiguity of current identification for the composition and structure of SEI. Beyond the elemental contents and the single- or double-layer structure, there is an expectation to obtain more detailed information about SEI [9,10], such as the morphology and spatial distribution of each species. Secondly, there is a lack of a unified and widely accepted method for the quantitative and comprehensive characterization of SEI properties, which further hampers the identification of key SEI properties that influence the specific performance of Li metal batteries. To promote a rational approach to the development of electrolyte design strategies, it is essential to establish a blueprint for a high-performance SEI, encompassing advantageous components, ideal structures, and key properties, and to establish a reliable structure-property relationship for SEI by combining experimental tools and machine learning.

Conflict of interest The authors declare no conflict of interest.

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